Tc-99 radiochemistry in Risø/RAS

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Tc-99 RADIOCHEMISTRY IN RISØ/RAS

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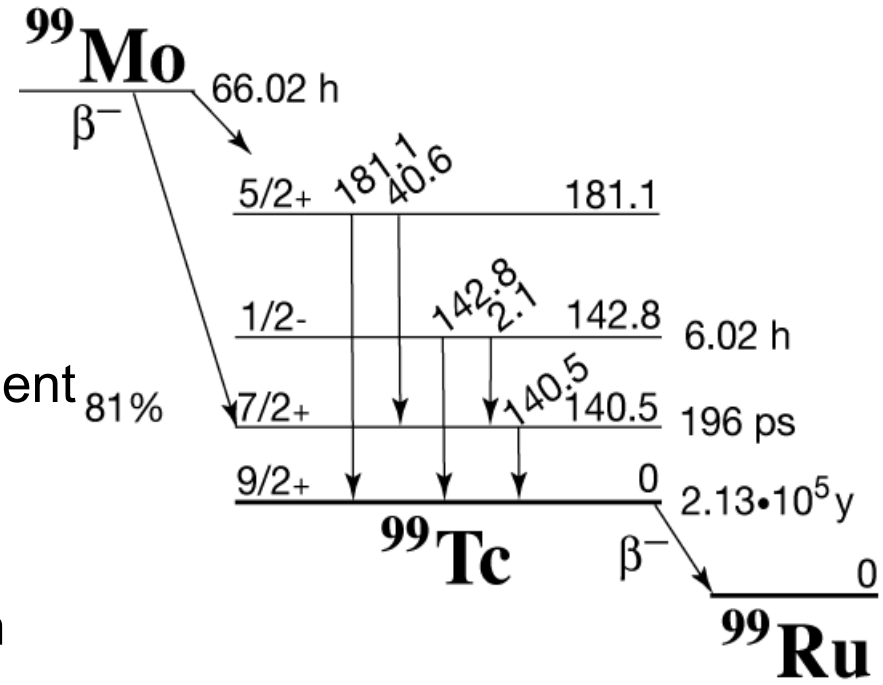
Technetium as an element

- Main isotope Tc-99
  - Long half life; 211000 y
- Oxidation states from -1 to +7
- Almost totally anthropogenic element
- Occurs in nature only minute amounts by
  - spontaneous fission product in uranium ore
  - neutron capture in molybdenum ores
- Chemically between rhenium and manganese; chemistry close to Re



- Main emission of Tc-99 is β^- with 294 keV

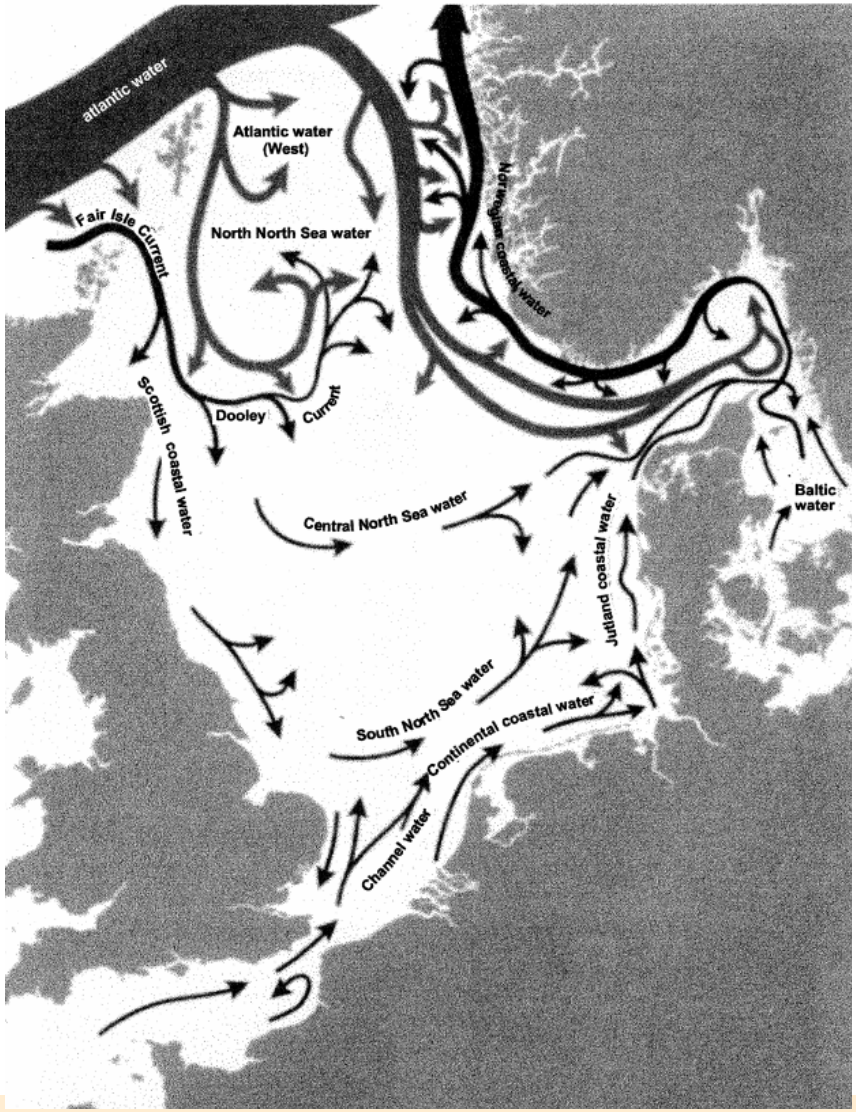
Tc-99 in the environment

- Main sources of environmental Tc-99 are:
  - nuclear fuel cycle; primarily by fuel reprocessing (Sellafield and La Hague)
    - In Sellafield EARP technology started in 1994 increased Tc releases
    - La Hague releases decreased after the 1980's
  - nuclear weapon tests
  - diagnostic nuclear medicine (minor)
- Tc-99 is present mainly in marine environment due to controlled process discharges to seas
- Exists in oxic marine conditions as pertechnetate ion TcO_4^-
  - very soluble species; low Kd to sediments
- Reduces from Tc(VII) to Tc(IV) in reducing conditions
  - affinity to particles increases

Tc-99 in the marine environment

- Interest towards Tc-99 research is high
  - mobile Tc (TcO_4^-) can be used as marine tracer
  - risks of escape of mobile Tc from nuclear waste repositories
- Levels of Tc-99 in sea water
  - fallout background in Atlantic Ocean ~ 0,005 Bq/m^3 [Dahlgaard et al. 1995]
  - North Sea and Norwegian coast (1996-1997): 0,8-8,5 Bq/m^3 [Brown et al. 1999]
  - Swedish west coast (2001) ~ 1 Bq/m^3 [Lindahl et al. 2003]
  - Baltic Sea; Finnish coast (1999) < 0,16 Bq/m^3 [Ikaheimonen et al. 2002]

Water circulation in the North Sea area



Anon 1993

Tc-99 speciation in the marine environment

- Behaviour of Tc in anoxic/reducing waters
  - Baltic Sea concentration drop
  - reduction of Tc and transfer from water column

- High Tc Kd values observed in some sediments (Techa river)
  - organic matter
  - anoxic conditions

- High uptake of Tc in brown algae
  - speciation

- New future activity in Risø/RAS

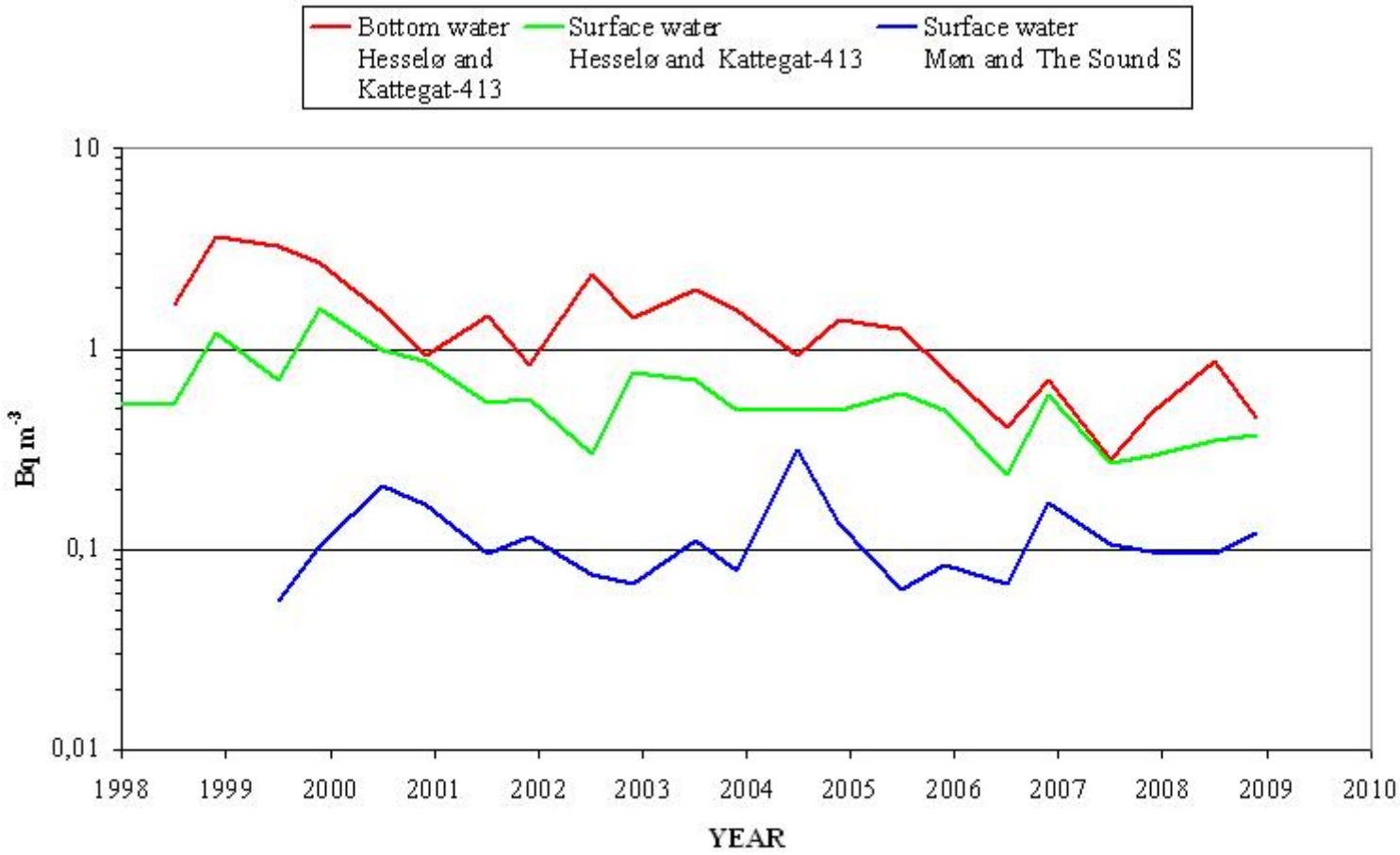
Tc-99 in soils

- Under oxidizing conditions in near-surface groundwater and soil Tc as TcO_4^-
  - soluble and stable over wide pH range
  - available for transfer to plants and biological processes
    - uptake mechanism?
- Insoluble species under reducing conditions
  - complexation with organic matter
  - some soil types together with wet conditions reduce Tc to be less available
    - soils with anion exchange capacity
  - anaerobic bacterial reduction
    - rice paddy fields

Monitoring of Tc-99 by Risø/RAS

- Long history of monitoring Tc
- Water and seaweed samples quarter-yearly from Danish waters
  - mainland
  - Faroe Islands
  - Greenland
- Water samples 200 L / analysis
- Seaweed samples
  - gram level for analysis

Tc-99 in seawater around Sjælland



Technetium-99 in seawater around Zealand, 1999-2009

Determination of Tc-99

- By radiometric methods using beta counting
  - liquid scintillation counting (LSC)
  - gas flow GM counting
  - neutron activation analysis

- By mass spectrometry
  - AMS
  - RIMS
  - ICP-MS

Radiometric methods vs. mass spectrometric methods

Table 9 – Comparison of radiometric and mass spectrometric methods for the determination of ^{99}Tc

Sample	Detection method	Target preparation	Detection limit	Sep. time[a]	Count time
Environmental sample	GM detector	Tc on disk	1.5 mBq	1–2 days/7 days	3–4 h
Environmental sample	LSC	Tc solution	17 mBq	1–2 days/7 days	2 h
Geological samples	RIMS	TcO_2	20 μBq	1–2 days	30–60 min
Water	AMS	Tc in Al_2O_3 or Nb_2O_5	6–10 μBq	1 days	20–40 min
Sediment, seawater	ICP-SFMS	Tc solution	0.16–0.29 mBq	1–2 days	10–20 min
Seawater	ICP-MS with ETV	Tc in solution	0.18 mBq	1–2 days	20–40 min
Environmental sample	ICP-QMS	Tc in solution	10 mBq	1–2 days	20–40 min
Environmental sample	ICP-SFMS on-line	Tc in solution	0.05 mBq mL^{-1} or 0.2 mBq	1 h/4–5 h	10–20 min

Hou and Roos 2008

Tc-99 determination in water samples by beta counting

- High purification from other radionuclides needed

- Main analytical steps (Chen method)
  - purification and preconcentration by anion exchange
    - Tc absorbs in column in neutral or alkaline pH
    - washing away especially Ru-103 and Ru-106
  - purification by Fe-hydroxide precipitation
    - Tc does not precipitate
    - removal of U, Th, Pu, Am, Po, Np
  - further purification with solvent extraction
    - by using TIOA (= tri-iso-octylamine) in xylene
    - back-extraction with NaOH
  - electrodeposition of Tc on steel disk for GM counting

A procedure used for 200 L water samples in Risø/RAS

200 L water filter + add Tc-99m tracer

AG1x4

- pass water through resin (22-23 h)
- wash with H_2O, NaOH-EDTA-NaClO (Ru decon.)
- wash with NaOH, H_2O, 1 M HNO_3

- strip with conc. HNO_3 + $NaNO_3$ (50 min)

Fe hydroxide precipitation

- evaporate strip solution to almost dryness
- add 5 M H_2SO_4 and dilute with H_2O
- add 15 % NaClO and heat for 10 min.
- dilute with H_2O to 30 mL
- add $AgNO_3$ + $FeCl_3$
- add NaOH -> pH 9
- heat + add NaClO

- filter the solution
- wash precipitate with water (pH 9)
- discard precipitate (U, Th, Pu, Am, Po, Np)
- add to filtrate 10 M H_2SO_4 + $K_2S_2O_8$
- dilute to 50 mL with H_2O

extraction

- extract with 10 % TIOA
- wash 2 times with H_2O (U+Th decon.)
- back-extract with 2 M NaOH
- back-extract with 0.5 M NaOH

- evaporate for el. deposition
- measurement with GM counter

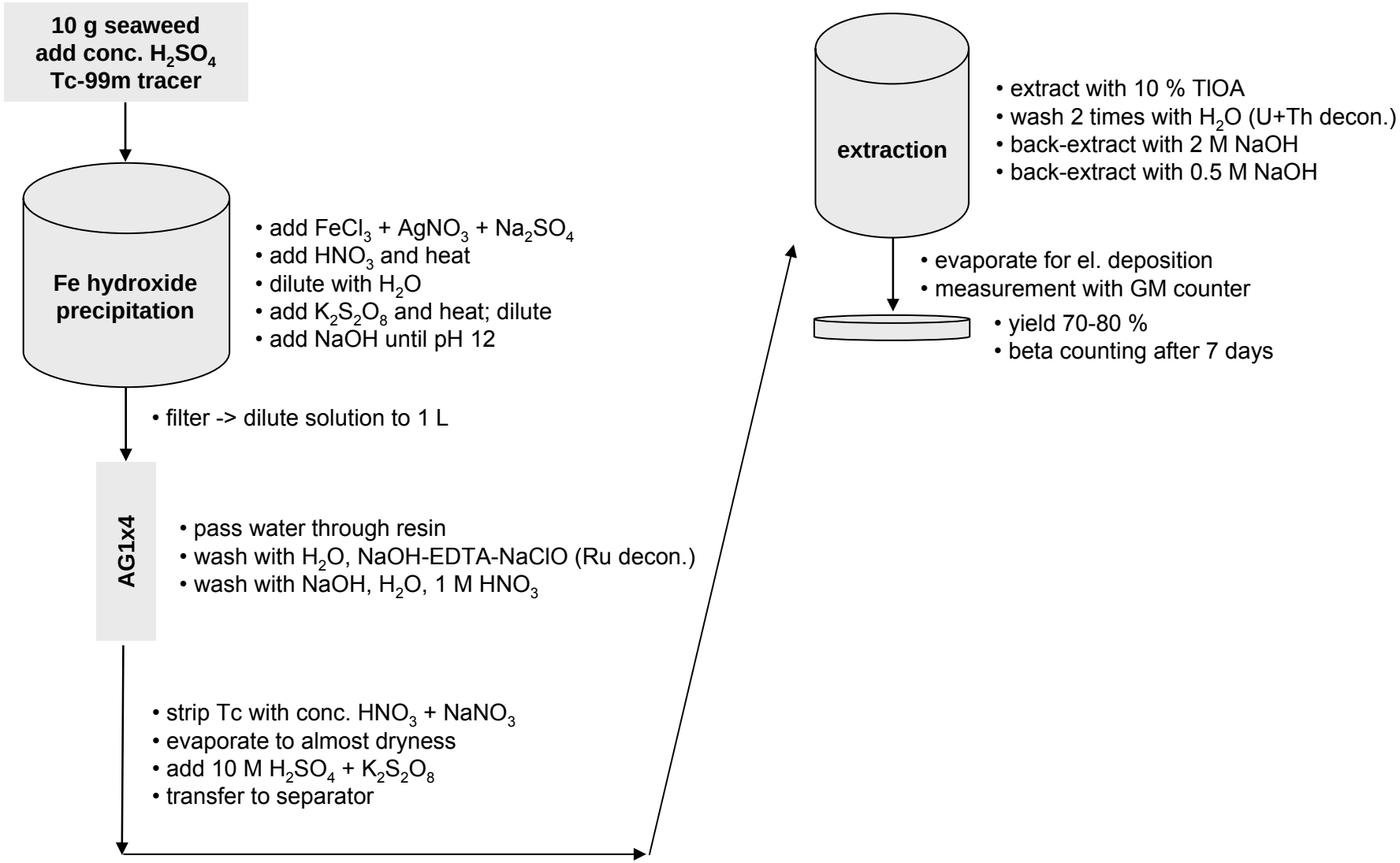
- yield 70-80 %
- beta counting after 7 days

- Procedure takes ca. 3 working days
- Determination limit 3 mBq/m^3

Tc-99 determination in seaweed samples by beta counting

- High purification from other radionuclides needed
- Main analytical steps (Chen method)
  - purification by Fe-hydroxide precipitation
    - Tc(VII) does not precipitate
    - removal of U, Th, Pu, Am, Po, Np
  - purification and preconcentration by anion exchange
    - Tc(VII) absorbs in column in neutral or alkaline pH
    - washing away especially Ru-103 and Ru-106
  - further purification with solvent extraction
    - by using TIOA in xylene
    - back-extraction with NaOH
  - electrodeposition of Tc on steel disk for GM counting

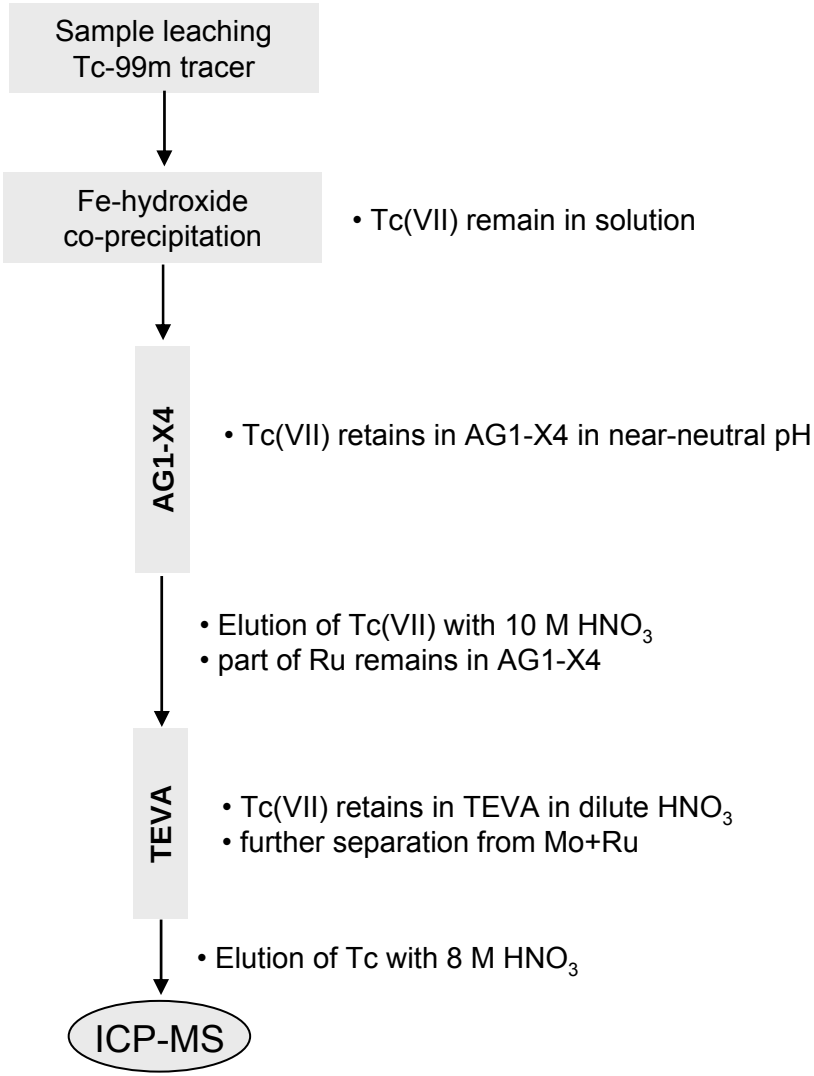
A procedure used for seaweed samples in Risø/NUK



Tc-99 determination in soil by mass spectrometry

- Main analytical steps:
  - Fe hydroxide precipitation
    - removal of impurities
    - Tc(VII) remains in solution
  - Anion exchange
    - purification and preconcentration
    - Tc(VII) absorbs in the resin
  - TEVA extraction chromatography
    - purification from Ru and Mo
    - Tc(VII) absorbs in resin
  - measurement with ICP-MS

A procedure for determining Tc-99 in water/soil with ICP-MS



- Procedure takes 1-2 working days
- Determination limit 0,3 mBq/m^3
  - depends on ICP used

Interfering species in determination of Tc with ICP-MS

Table 8 – Potential interfering species on mass 99 in ICP-MS

Isobar/tailing	Oxide	Hydride	Argide	Chloride
^{99}Ru (12.7%)	^{83}Kr^{16}O (11.5%)	^{98}MoH (23.8%)	^{59}Co^{40}Ar (100%)	^{62}Ni^{37}Cl (3.6%)
^{98}Ru (1.1%)	^{81}Br^{18}O (49.5%)	^{98}RuH (1.9%)	^{63}Cu^{36}Ar	^{64}Zn^{35}Cl (48.6%)
^{100}Ru (12.6%)	^{67}Zn^{16}O$_2$ (4.1%)		^{43}Ca^{16}O^{40}Ar	
^{98}Mo (24.1%)	^{51}V^{16}O$_3$ (99.8%)		^{40}Ca^{18}OH^{40}Ar	
^{100}Mo (9.6%)				

- In low-Tc samples determination limit is hampered due to interfering species as the signal intensity is small
- Main interferences Ru-99 and hydride of Mo-98
  - Ru can be calculated from Ru-102
    - still the presence of Ru is a problem in low activity samples

Other methods for determination of Tc

- Lund method
  - wet ashing + ashing (with ammonia)
  - Fe hydroxide precipitation
  - removal of radiocesium with AMP
  - oxidation of Tc to Tc(VII) and extraction with TBP
    - HF to complex other elements
    - back-extraction with NaOH
  - electroplating of Tc
  - determination limit ~ 1,2 mBq/sample

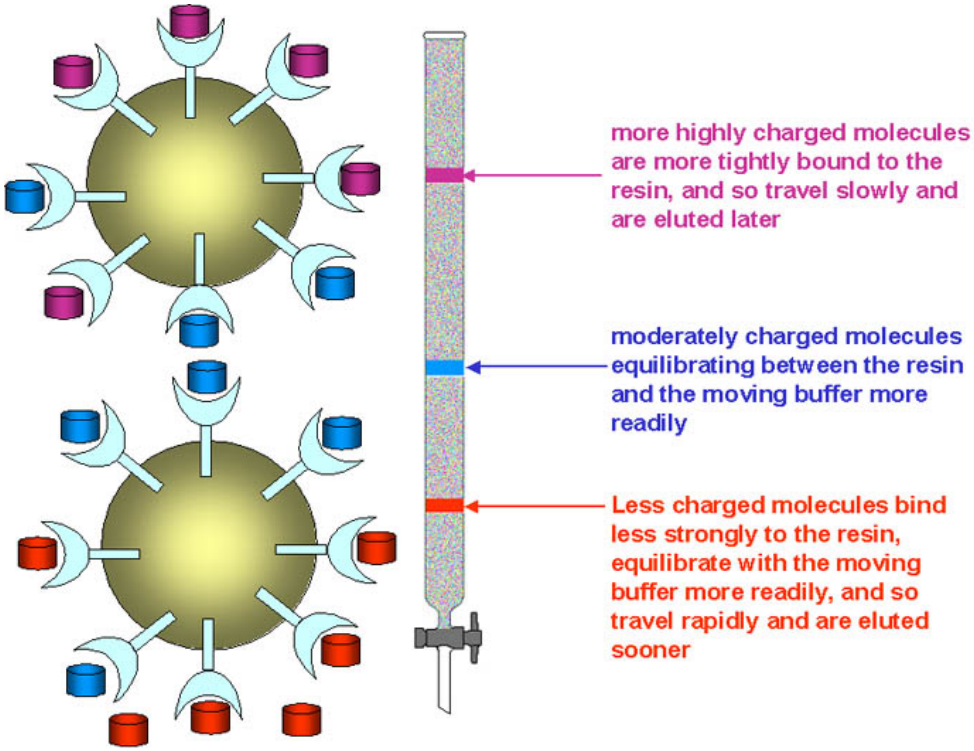
Other methods for determination of Tc

- Southampton method
  - ashing (up to 550 ˚C) -> dissolution of Tc with 8 M HNO_3
  - Fe hydroxide precipitation
  - anion exchange
    - removal of calcium, Co-60, Ni-63, Sr-90, Cs-137
  - extraction with TnOA in xylene
    - Ru in water phase
  - organic phase with Tc to LSC solution
    - counting after 1 week (Tc-99m dies away)
  - determination limit 1,7 mBq/m^3

Other methods for determination of Tc

- Harvey method
  - filtered sea water sample; addition of Re carrier
    - Re used as yield determinant
  - anion exchange
  - destruction of Tc-containing organic resin by heating
    - dissolution in HCl
  - Fe hydroxide precipitation
  - anion exchange
    - elution of Tc and Re with alkaline sodium perchlorate solution
  - sulphide precipitation of Tc and Re -> dissolution
  - precipitation of Tc and Re tetraphenylarsenium salt
    - gravimetric yield determination
    - measurement with proportional counter
  - determination limit for 100 L water sample 140 mBq/m^3

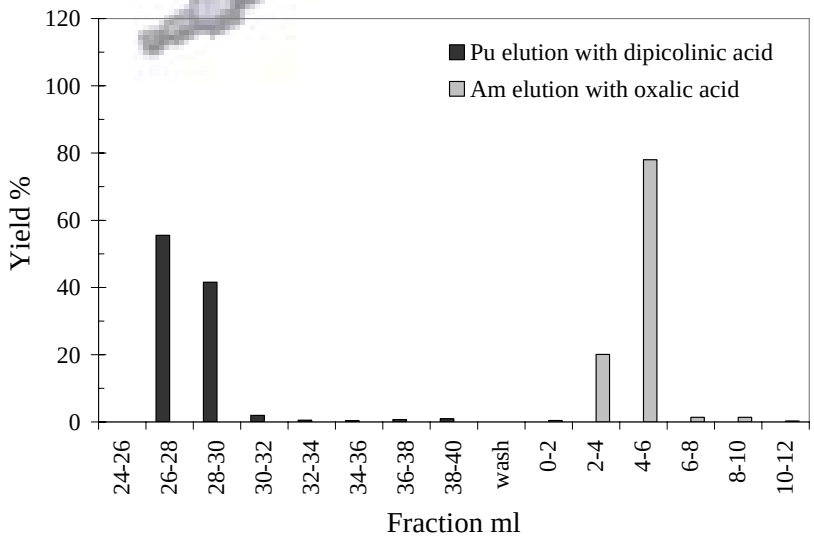
Ion chromatography

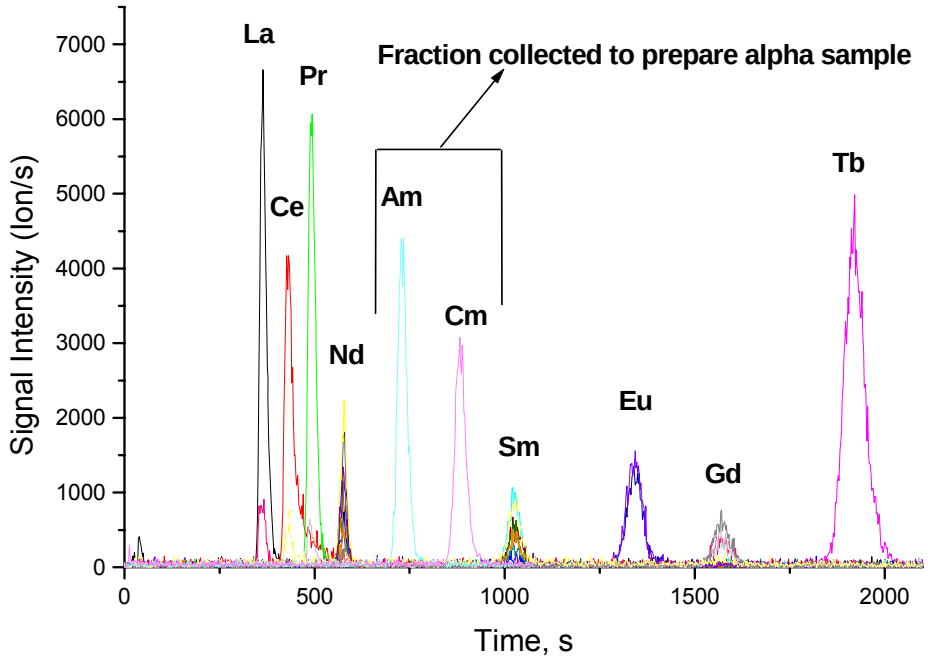


- Why?
  - to elute Tc fraction being free from Mo and Ru
- Suitable complexing agent to create separation
  - suitable chemistry (pH and ionic strength)
  - suitable elution speed

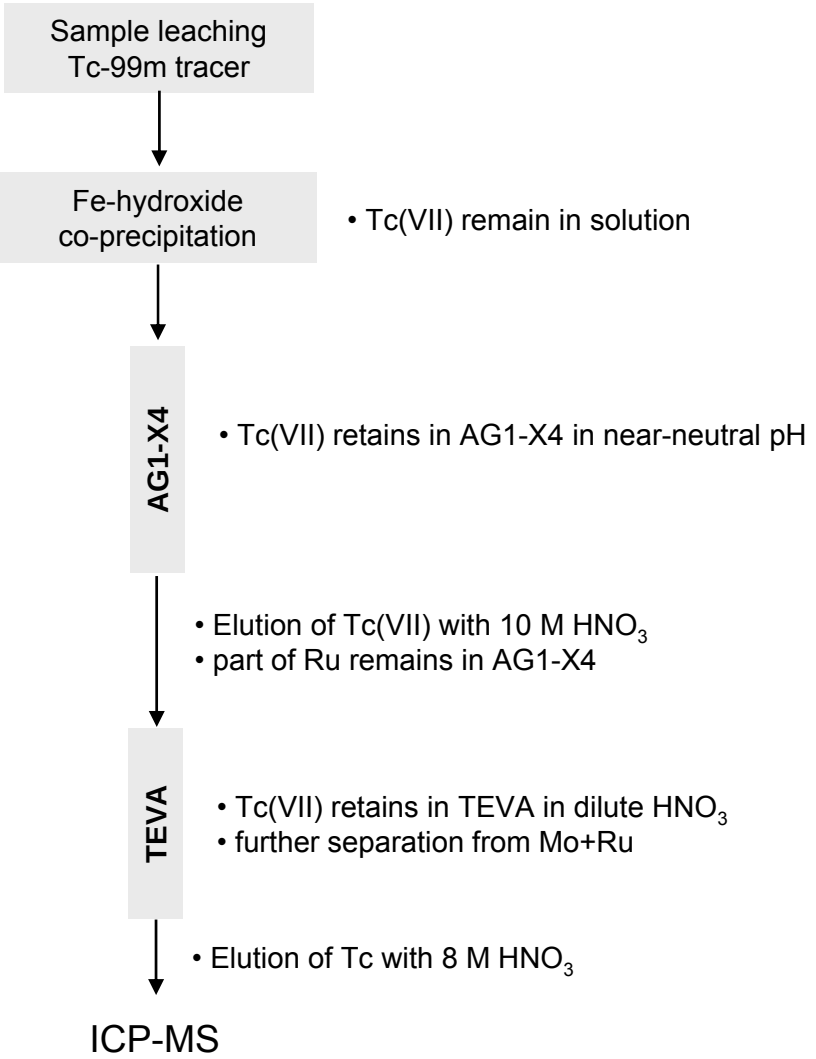
Dionex CS5A column and its previous use for radionuclides

- Mixed-bed column for transition metals
- Separation of Am and Cm from lanthanides for alpha spectrometry
- Separation of Am and Pu





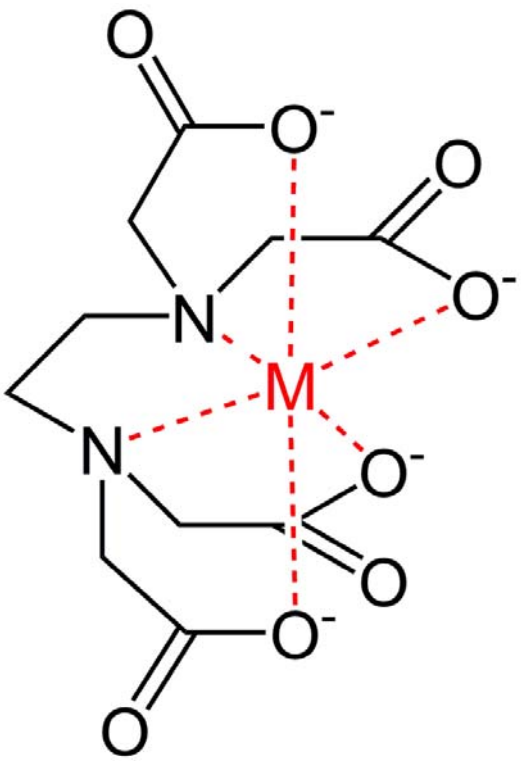
Purification of Tc from Mo and Ru



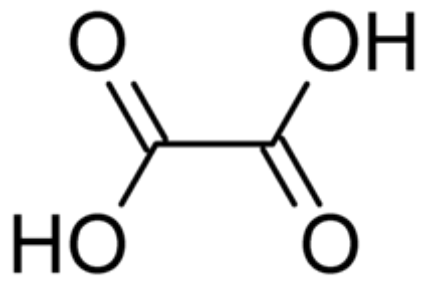
- Use of complexing agents
  - EDTA
  - Dipicolinic Acid (PDCA)
  - Oxalic Acid
- Chromatographic separation of Tc prior to MS
- Sample free from interfering Mo and Ru
- Tc both in reduced and oxidized forms

Complexing agents

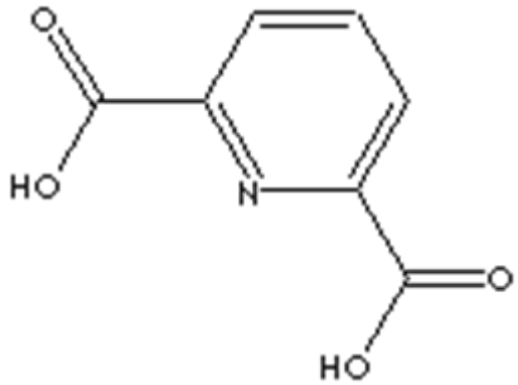
EDTA



Oxalic acid



PDCA

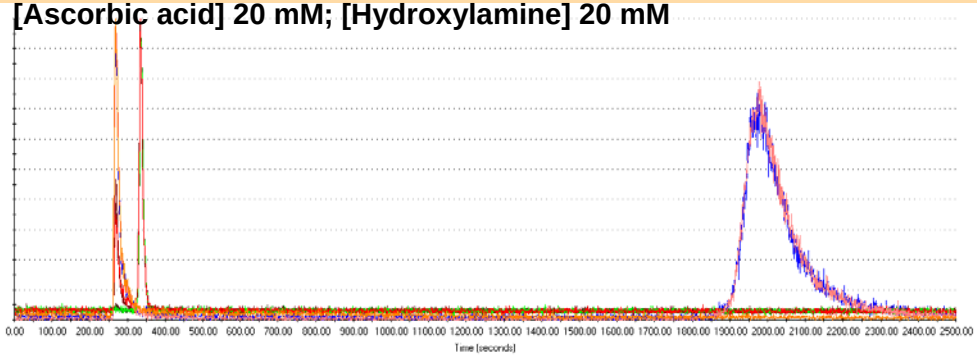


Reduction of Tc

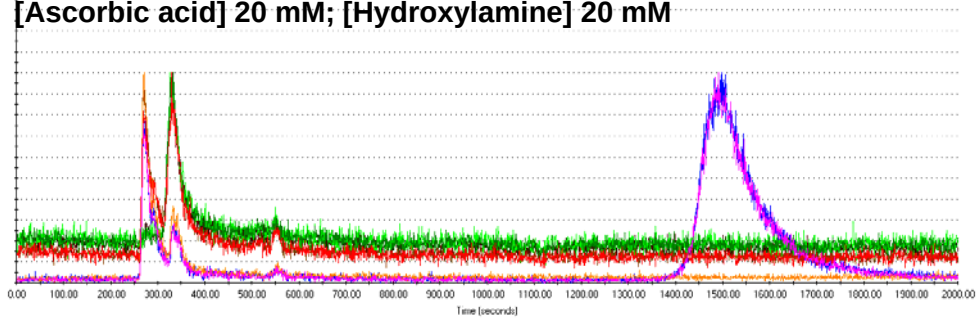
- 20 mM ascorbic acid + 20 mM hydroxylamine
- 25 min reduction time

- EDTA and oxalic acid positive
- PDCA does not elute all Tc

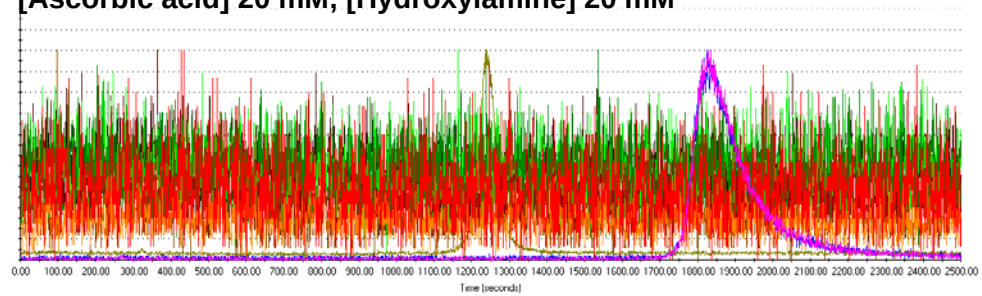
[EDTA] 0,1 M; pH 7,0; [Na2HPO4] 50 mM; [Na3PO4] 50 mM
[Ascorbic acid] 20 mM; [Hydroxylamine] 20 mM



[Oxalic acid] 0,15 M; pH 4,2; [CH3COOH] 75 mM; [CH3COONa] 75 mM
[Ascorbic acid] 20 mM; [Hydroxylamine] 20 mM

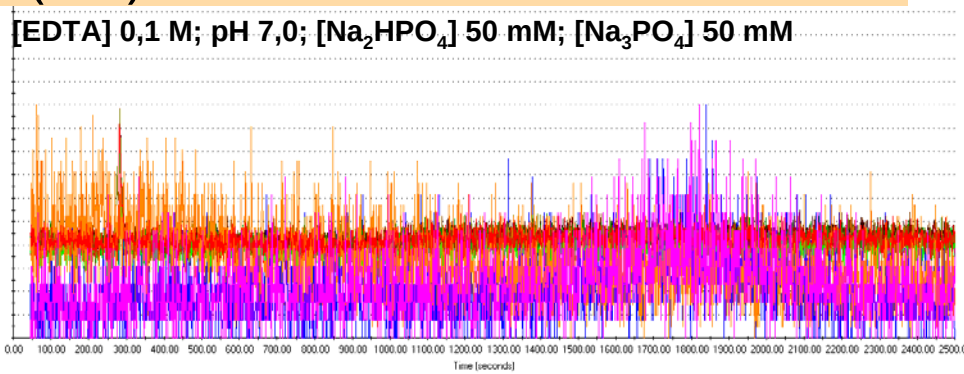


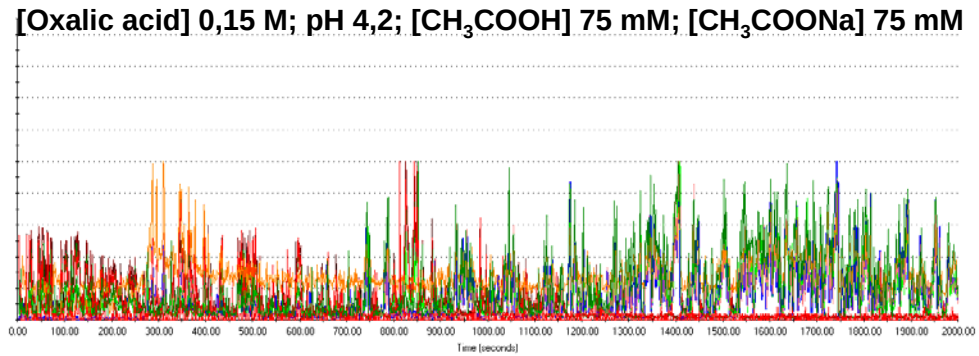
[PDCA] 50 mM; pH 4,65; [CH_3COOH] 75 mM; [CH_3COONa] 75 mM
[Ascorbic acid] 20 mM; [Hydroxylamine] 20 mM

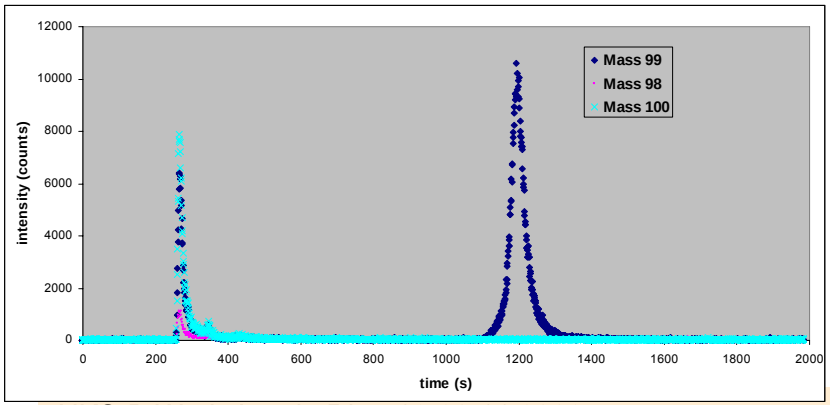


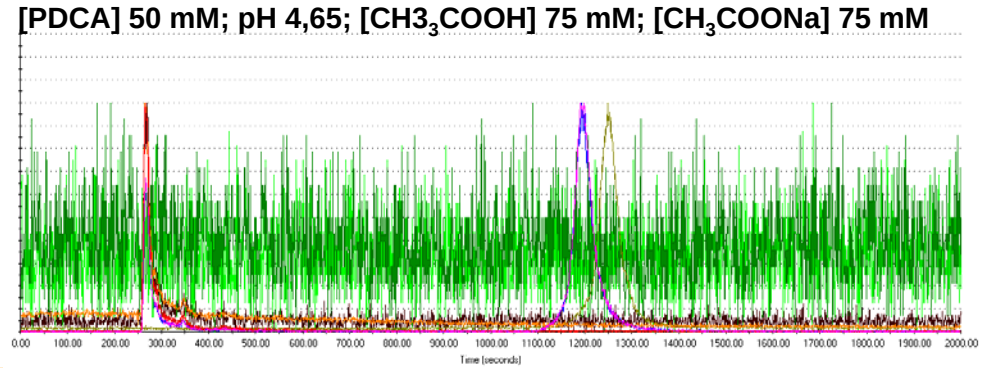
No reducing agents; Tc as Tc(VII)

- EDTA and oxalate show no ability for elution of Tc or Mo and Ru
- PDCA complexes strongly -> full separation from Ru
  - No elution of Mo

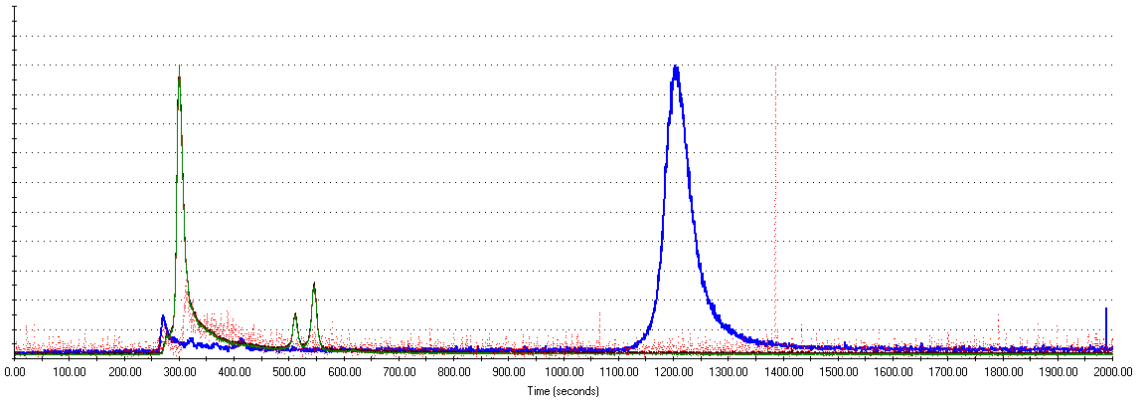




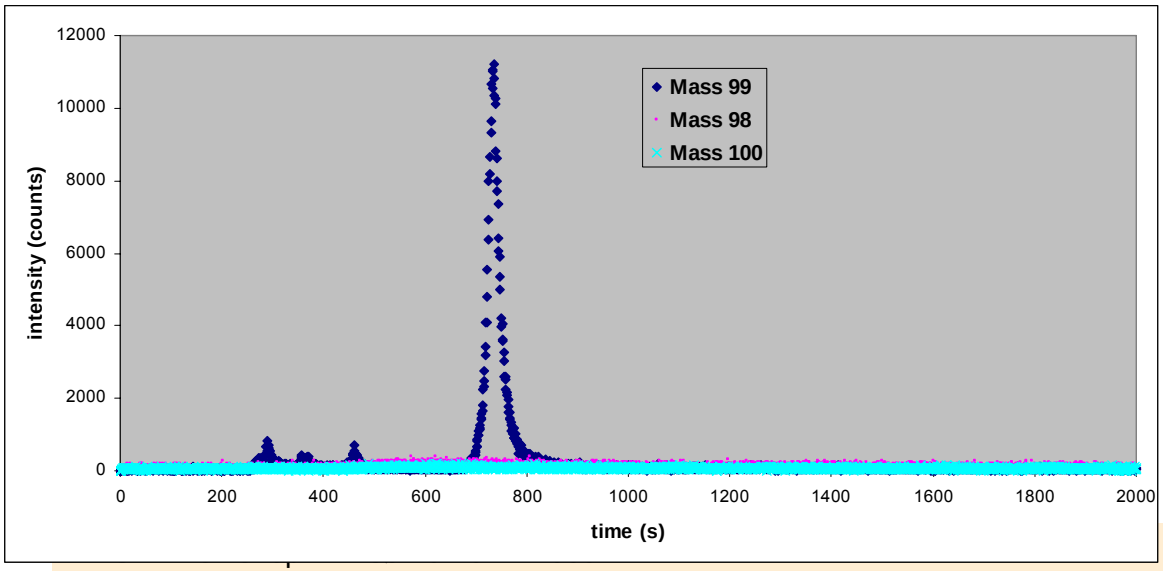




Results with soil sample



- elution with oxalate



- elution with PDCA

Thank you for your attention!